Carbon Materials From Coal

Frank Derbyshire

Center for Applied Energy Research
3572 Iron Works Pike
University of Kentucky
Lexington, KY 40511-8433

INTRODUCTION

The production and consumption of coal is overwhelmingly directed to its use as a fuel for the generation of heat and power. At the same time, coal also represents a significant resource for the production of chemicals and carbon materials. Although, in this context, the current importance enjoyed by coal is much less than in former times, it can be anticipated that the non-fuel uses of coals will increase in years to come: coal is the most abundant fossil fuel; it is globally available; it is obtained at low cost; and the structure of coal is suited to the production of a broad range of products.

This paper will consider how the structure and composition of coals of different rank and origin can give rise to carbon materials with very different properties and fields of application. While the markets for these products can only have a small direct impact on coal consumption, they can exert a considerable indirect influence through materials applications that enhance the clean efficient use of energy. Examples include the control of emissions through adsorption and catalysis, energy storage devices and delivery systems, and the fabrication of strong lightweight structures for various forms of transport.

STRUCTURE OF COAL AND CARBONS

The ability to produce a spectrum of carbons from coal can best be understood in relation to its basic structure. As depicted in a model developed by Oberlin[1], coal consists of relatively low molecular weight structural units that are connected by different types of chemical bond. The structural units tend to be planar and consist of cyclic carbon (aromatic and hydroaromatic) and heterocyclic rings. Attached to the rings are alkyl, and oxygen and sulphur-containing groups. The structural units are connected by covalent (alkyl, or etheric - oxygen, and sulphur - bridges) and non-covalent bonds, hydrogen bonds and van der Waals forces. A proportion of weakly bonded or physically trapped material is also present, some of which can be extracted by solvents. While the overall structure is amorphous, there are limited regions of short-range order that are defined by the parallel alignment of two (or more) structural units.

As the rank of the coal increases, there are changes to the structure that include: an increase in aromaticity and a reduction in aliphatic content; the elimination of oxygen functionalities; and changes in the nature of the connecting linkages between structural units - a decrease in the extent of hydrogen bonding and covalent linkages, and an increase in aromatic-aromatic interactions[2,3]. There are accompanying changes in the spatial arrangement of the structural units that improve the extent of short-range order: increases in the average number of atoms per structural unit, in the number of structural units or layers that are aligned in parallel, and in the mutual orientation of sets of parallel layers[4]. The model predicts, as confirmed by other studies, that coals posses inherent porosity, and that with increasing rank, the pore structure becomes narrower.

For the production of some carbon materials, coal serves simply as a source of elemental carbon and its structure and composition are not of any great relevance. These processes tend to involve high energy input, and the rearrangement of carbon atoms and carbon fragments in the vapor phase, or via vapor-solid reaction, to produce highly ordered carbons such as fullerenes and nanotubes[5,6] and filaments[7]. However, in the majority of cases, the conversion process takes advantage of the structure of coal with the aim either of preserving its amorphous configuration or of promoting increased structural order.

With the exceptions of diamond, diamond-like materials, and closed-cage structures (fullerenes and nanotubes), the structure of most carbons is related to that of crystalline graphite. Nascent elements of the graphite structure are recognizable in coal in the form of planar cyclic carbon structures, and their propensity for parallel orientation. Upon the thermal treatment of coals (or any other solid or liquid carbonaceous precursor) the thermodynamic driving force is towards improved structural order through the aromatization, growth and alignment of structural units. The potential for ultimately producing a graphitic structure is determined by the changes that occur between about 400-600°C, as illustrated in Figure 1. The formation of crosslinks between structural units can impede improvements in structural order, preserving the random order present in the parent coal, and resulting in a hard, porous, isotropic char. Such materials are termed non-graphitizing carbons, as there is little further improvement in crystalline growth and ordering upon heat treatment to temperatures as high as 3000°C. Low-rank coals, oxidized bituminous coals, and anthracites follow this pathway.

Under conditions where there is minimal crosslinking, the formation of a fluid state allows planar aromatic structures to grow in size and diffuse into positions of parallel alignment, leading to the nucleation and growth of a separate anisotropic phase within the parent isotropic liquid. The anisotropic phase is a liquid crystal known as carbonaceous mesophase. If continued, the process is eventually arrested by solidification of the melt. The anisotropic carbon content of the resulting char is determined by the precursor composition and carbonization conditions, and the duration of the fluid phase. In the carbonization of (bituminous) coking coals and coking coal blends, mesophase development is limited because, in the coke oven, there is a mixture of fluid and solid phases, and the heating conditions are such that the existence of the plastic condition is transient. The char or coke consists of a mixture of isotropic, and small and larger anisotropic regions: in the terminology of optical microscopy, mosaic and flow domains, respectively. With pitch precursors, a fluid condition can be maintained for longer periods, allowing the possibility of extensive mesophase development through the continued formation of nuclei, their growth and coalescence. The highly anisotropic chars thus produced are composed of small, well-ordered pseudo-graphitic crystallites that are oriented with their basal planes in approximately parallel orientation. They are weaker, due to the low density of crosslinks, and are of lower porosity than isotropic chars produced from thermosetting precursors. These are graphitizing carbons, which experience a sharp improvement in structural order and crystallite size upon heat treatment to temperatures above about 2200°C.

DIRECT CONVERSION OF COALS TO CARBONS
Activated Carbon
In the production of activated carbons from coal, it is desirable to preserve, as far as possible, the amorphous nature of the parent coal structure: the porosity of activated carbons derives from the small size of the constituent disordered crystallites and their random packing. As discussed, this is achieved via crosslinking reactions during low-temperature carbonization. Low-rank coals and anthracites can be processed directly, while the thermoplastic behavior of bituminous coals is first suppressed by air oxidation, or other means such as the use of additives or coal blending.

Coals are carbonized at 500 - 700°C to produce isotropic chars with pore structures that reflect those of the starting coals. However, partly because of volume contraction that is caused by heat treatment, most of the pores are closed or too narrow to be of practical value. Porosity is then developed by activation in which carbon is removed through controlled gasification at 800-1000°C in steam or CO_2. The pore structure in the final carbon product is therefore not created but is a development of the basic structure that is inherent to the starting material and translates through the processes of carbonization and activation. For this reason, activated carbons produced from coals of different rank reflect the same changes in pore size distribution as do the original coals: those from low-rank coals have high mesopore volumes, those from bituminous coals have a broad pore size distribution, and those from high rank coals are microporous. Together, coals and lignite constitute about 50% of the raw materials used to manufacture activated carbons. They are produced with a broad range of product properties, in the form of both powders and larger sized products (granules, pellets or extrudates).

Activated carbons with novel properties can be produced from coal by chemical activation using KOH. Extremely high surface area carbons can be produced from bituminous coals and petroleum coke precursors by reaction with KOH at temperatures up to 1000°C, followed by leaching to recover the reagent[8]. Despite the unusual properties of this activated carbon (surface area > 3000 m^2g^{-1}, and total pore volume 2.0 - 2.6 ml/g), only limited quantities have been produced. The cost, low bulk density, and difficulties in handling have presented obstacles to successful commercialization, although a recent development has allowed the powder to be incorporated into a more tractable monolithic form[9]. In variants of the same process, KOH has also been used to produce high surface area, hard extruded carbons from low-rank coals[10] and preoxidized bituminous coals[11], high surface area activated mesocarbon microbeads (see below)[12,13], and catalysts with high activity and selectivity for the hydrodehalogenation of halogenated aromatic compounds - reactions that are of interest for environmental protection[14,15].

Metallurgical Coke
The manufacture of metallurgical coke represents the single largest non-fuel use of coal for the production of a carbon material, accounting for approximately 10% of world coal consumption. The phenomenon of fluidity development in coking coals and coking coal blends is critical to producing the characteristics required of metallurgical coke. An associated outcome is the development of anisotropy through mesophase formation. Its significance to many of the properties of coke that are of importance to metallurgical practice is a matter of some debate, but it does appear to influence coke strength[16].

CARBONS FROM COAL-DERIVED LIQUIDS
The range of carbons that can be obtained from coal is considerably expanded through the derivation of high molecular weight liquids or pitches. Liquids can be obtained by a number of different methods, such as solvent extraction, hydropyrolysis, direct liquefaction, and coking, each of which effectively serves to liberate the coal structural units. The composition of the liquids can be altered to a greater extent through the selection of the coal and reaction parameters, allowing

considerable latitude in the preparation of precursors for different end-products.

Isotropic and Mesophase Pitch Carbon Fibers

Different types of carbon fibers can be classified according to the precursor or process method: polymers, rayon and polyacrylonitrile (PAN); vapor-grown; and pitch. The last of these groups is divided into fibers produced from isotropic pitch, and from pitch that has been pretreated to introduce a high concentration of carbonaceous mesophase. The former are so-called general purpose fibers that are sufficiently strong to be used in a wide range of applications, while the latter are high performance materials, possessing very high tensile strength and modulus. Extensive discussions of the synthesis and applications of isotropic pitch-based and mesophase pitch-based carbon fibers has been given by Edie[17], and Singer[18] has written a more general account of carbon fiber technology .

The production of isotropic pitch-based carbon fibers by melt-blowing was first commercialized in 1970, using a pitch prepared from ethylene cracker tar. Subsequently, commercial processes were developed to produce isotropic fibers from coal-tar pitch, and petroleum pitch prepared from decant oils produced by fluidized catalytic cracking[see19]. During the 1970's, the National Coal Board (now the British Coal Corporation), United Kingdom, conducted extensive research on the formation of continuous carbon fibers from coal extracts produced by a liquid solvent extraction process, LSE[20]. Although the starting material was isotropic, the aim was to produce fibers with high strength and modulus, and a final high temperature heat treatment step under tension was used to improve fiber strength - a technique that has also been applied to rayon-based and isotropic pitch carbon fibers[18]. Although these fibers were unable to compete with the later-developed PAN and mesophase fibers, the work demonstrated that other sources of coal liquids could be used as effective fiber precursors. Recent work has shown that continuous filaments of isotropic carbon fibers can be produced from coal liquefaction products[21,22].

The discovery of carbonaceous mesophase in the 1960s[17,18] led to the development of mesophase fibers, in which the orientation of the molecular structure along the fiber axis allows the development of a graphitic structure. Because the intermolecular interactions in the liquid crystal phase are so weak, they can be oriented by any small shear force such as in extrusion or elongation, to produce an oriented fiber. Moreover, the orientation and resulting structure can be modified by spinning conditions, and especially the spinnerette design.

The preparation of the starting material for isotropic and mesophase pitch fibers involves quite different treatments. For isotropic pitch fibers, the principal steps involve the removal of volatile components by distillation, and solids separation. Distillation increases the softening point and aromaticity of the pitch. For mesophase fibers, the pitch must be further treated in one of several different ways to generate a high mesophase content product that is suitable for melt spinning. Spinnability is a critical requirement, since the production of continuous filaments is essential for most applications of high performance fibers. In both cases, the as-formed, "green" fibers require to be stabilized to render them thermosetting before carbonization. Stabilization is normally accomplished by air oxidation, with a weight gain of up to 10%. The introduction of oxygen functionalities leads to the formation of crosslinks during oxidation and subsequent carbonization. Oxidation must be initiated at temperatures below the glass transition temperature of the fibers to prevent melting, and for mesophase fibers, to prevent loss of molecular orientation. With continuing reaction, oxidative crosslinking progressively raises the glass transition temperature, such that the reaction temperature (and rate) can be increased. Eventually, the glass transition temperature is sufficiently elevated that pyrolysis reactions precede plasticity development, and the fibers can be carbonized.

To develop strength, the stabilized fibers are carbonized in inert atmosphere at temperatures up to about 1200°C. This is the final chemical processing step for isotropic fibers: due to the lack of molecular orientation, there is little further gain in strength upon heat treatment to higher temperatures. Conversely, there are large increases in the tensile strength and modulus of mesophase fibers upon graphitization (up to 3000°C). The final fiber properties are determined by the degree of orientation of layer planes along the fiber axis, and the size and perfection of individual crystallites. The modulus of isotropic fibers is about 1/20 of that of mesophase fibers, while their tensile strength is around 1/3.

Lower cost makes isotropic pitch fibers attractive for applications where high tensile strength or modulus are not required. Examples include: enhancing the properties of composite friction materials; the reinforcement of engineering plastics; ablation materials; acoustic and thermal insulation; electrically conductive fillers for polymers; electromagnetic shielding; filter media; paper and panels; the production of hybrid yarns with other fibers; reinforcing concrete to improve flexural strength and other properties; and as potential replacements for asbestos. Mesophase pitch fibers are used in advanced composite materials. Graphitized mesophase pitch fibers tend to have higher modulus and lower tensile strength than the PAN-based equivalents: the former have advantages in applications requiring high stiffness, high electrical and thermal conductivity, low thermal expansion, and high temperature oxidation resistance, while the latter are employed where high strength is required. Because of their high modulus, mesophase fibers are often used in

aerospace structures, and the very high thermal conductivity of recently developed fibers has opened applications for heat dissipation in areas such as high speed machinery, aircraft structures, and electronics.

Activated Carbon Fibers
There is a growing interest in the development and application of activated isotropic carbon fibers (ACF). They can be produced with high surface area, and the narrow fiber diameters (usually 10 to 20 microns) lead to much faster adsorption, desorption, or catalytic reaction than for granular carbons. The novel properties of ACFs make them more attractive than other, more conventional activated carbons for certain applications[19]. In this laboratory, we have examined the synthesis of isotropic pitch fibers and activated fibers from non-conventional pitches. Whereas most commercial ACFs are microporous, activated carbon fibers produced from shale oil asphaltenes and from coal liquefaction products are found to possess high mesopore volumes[21,22]. Through the selection of appropriate precursor pitches, it is possible to produce ACFs with substantially different properties in terms of pore size distribution and surface chemistry, as well as potentially allowing more rapid processing. In this context, coals present a fertile resource as heavy coal liquids can be produced relatively cheaply, and with a wide range of composition.

Individual fibers (and powders) present difficulties in handling, containment, and regeneration, and in fixed bed operations they would present an unacceptably high pressure drop. These problems can be surmounted by their incorporation into forms such as felt, paper, woven and nonwoven fabrics, and rigid monolithic structures. Potential advantages of the monolithic forms are: they allow facile handling; they can be highly permeable; they permit the possibility of regeneration; where there is good contact between the carbon constituents and if they are adequately conducting, electrical energy can be used as a method of rapid and uniform heating to drive the processes of desorption or regeneration[23-26]; and they can be fabricated to a given size and shape, a consequence of which is that completely novel adsorber/reactor designs are possible.

In this laboratory, we have developed rigid activated carbon fiber composite materials[27,28]. Using pre-activated carbon fibers, 80-90% of the surface area of the free fibers is retained in the composite. Alternately, the formed composite can be carbonized and activated in steam or carbon dioxide. The composites are strong, highly permeable to fluids, and can be machined. They can be used to efficiently separate CH_4 and CO_2[28]. In liquid and gas phase column tests, the composites have been compared to commercial granular activated carbons, where it has been found that there is much more effective use of the adsorptive capacity of the carbon before column breakthrough. The higher efficiency of the composite is attributed to: the uniform structure which ensures that the feed is distributed evenly through the column: the presentation of the adsorbent surface in fiber form which allows high rates of adsorption; and the open architecture which renders the pore structure readily accessible.

Mesocarbon Microbeads
By arresting the process of mesophase development at the nucleation stage, mesophase microbeads can be obtained by separation using techniques such as centrifugation and solvent extraction. The diameter of the beads is typically in the range 1 - 80 μm[12,13]. The microbeads are used in the "green" form to produce so-called sintered or binderless carbons[29]. These are high density, high strength, shaped carbons that are formed by molding the microbeads. Upon carbonization, strong bridging bonds are created at the points of contact between the microbeads. Under applied pressure, deformation of the microbeads helps to minimize the porosity of the resulting artefact. Heat treatment to graphitizing temperatures greatly enhances strength and produces a material that is composed of graphitic microbeads but is macroscopically isotropic due to their random orientation. Carbonized and graphitized microbeads are used in the production of new composite materials, including electrode materials for Lithium batteries. The various applications of the microbeads take advantage of the basic properties of graphite - high resistance to corrosion and oxidation, and excellent electrical and thermal conductivity.

Needle Coke
Highly anisotropic cokes are obtained by solidification after extensive mesophase development. The structure renders them relatively friable or "soft", with low porosity, and the anisotropy is reflected in the acicular shape of the coke particles, which are termed needle coke. Needle cokes are readily graphitizable and are used for the manufacture of graphite electrodes for arc-steel furnaces. Normally, needle coke is produced from selected petroleum feedstocks: one example is decant oils from fluid catalytic cracking. Feedstock properties such as high aromatic carbon content are important. The aromatic character of coals implies that they could present an attractive alternative source for the production of needle coke, and it has been shown that highly aromatic, pretreated coal tar pitches can give excellent needle cokes. It has further been demonstrated that a suitable needle coke can be obtained from coal via solvent extraction[30]. Bituminous coal is slurried with about three times its mass of anthracene oil (itself a product of coal tar distillation), and heated to 415°C for 60 min at 0.8 MPa (autogenous pressure), when approximately 70-80% of the coal (dmmf) is solubilized. The mineral matter and undissolved coal are separated by hot pressure filtration to afford a coal extract solution (filtrate) containing around 0.1% ash. The extract is then preheated to ~ 520°C and fed to a delayed coker to produce needle coke, and the coker overhead is

recycled as solvent. The process has been successfully demonstrated on a large scale in which sufficient coke was produced to fabricate graphite electrodes (using coal tar pitch binder) that were tested in a 25 ton steel production furnace[30]. Approximately 10% of needle coke is now produced from pretreated coal tar: annual world production is about 1.3 Mt.

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Figure 1. *Production of disordered and ordered carbons from coal*

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